FERRIC HYDROUS OXIDE SOLS
OF NARROW SIZE DISTRIBUTION

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FERRIC HYDROUS OXIDE SOLS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

SUMMARY

In the area of air pollution, test aerosols consisting of sized monodispersed particles are useful in dust inhalation studies, in meteorological dispersion tests, and in apparatus calibration. Monodispersed particles which can be easily produced in quantity would contribute significantly to activities in these areas. Previous research on metal hydrous oxide sols led to a method of producing monodispersed particles in the one to five micrometer range, and studies on iron corrosion led to the formation of near spherical ferric sulfate particles. The research reported herein was concerned with investigation of particle production parameters such as; temperature rise, length of reaction at 80°C, pH, and ratio of $[Fe^{+3}]$ to $[SO_4^{-2}]$ in order to establish the necessary conditions for producing monodispersed spherical particles on a large scale.

In all tests monodispersed ferric sulfate particles were formed, but a lowered pH caused a noticeable change in particle morphology. Spherical particles were not formed for any condition tested. The particles formed were truncated cubes with two opposing corners flattened. Ferrous sulfate crystals formed in a few tests; these appeared as thin needle-like crystals and were attributed to use of stored solutions which were one or two weeks old. It was hypothesized that the ferric ions had time to undergo reduction to the ferrous state. Fresh solutions consistently gave good cubical particles, and the method of production proved quick, easy, and reproducible.

It was determined that a linear relationship existed between parti-

cle size and reaction time. Therefore, the reaction time necessary to produce specific size particles can be predetermined.

A temperature rise of 1.5°C/min. was found to be an important parameter for particle production. To insure a linear temperature rise, a tubular complex with good heat transfer characteristics is suggested as a method for large scale production of the ferric sulfate particles.

Monodispersed ferric sulfate particles were produced and stored in distilled water. Spherical particles could not be generated by changing pH or molar ratios. Longer reaction times may contribute to increased sphericity. Large scale production appears feasible if good heat transfer and uniform heating can be obtained.

CHAPTER I

INTRODUCTION

Recent concern in the area of air pollution has created a greater need for test aerosols for use in air pollution monitoring and control. Such aerosols are used in the calibration of measuring apparatus, in studies related to the inhalation of particles, and in research on the chemical and physical properties of airborne particles. In activities where an aerosol is needed, it is advantageous to be able to use a monodispersed aerosol. A monodispersed aerosol is defined as one that contains particles all of the same size. Ideally, this would be an aerosol whose particles exhibit a standard deviation of zero and a geometric standard deviation of unity ($\sigma = 0.0$, $\sigma_g = 1.0$). Most mondispersed aerosols manufactured today have a finite standard deviation and a geometric standard deviation slightly greater than unity. Increased advantage accrues with aerosols of spherical particles. This advantage results from the fact that spherical particles do not change apparent surface area when examined in various orientations. The spherical characteristic makes them particularly useful in light scattering techniques for particle size analysis. The ability to form monodispersed particles of various sizes in situ would be advantageous as would the capability for accurately reproducing particles using relatively easy methods and with simple glassware and equipment. Where particles are frequently used, a capability for generation and storage of larger quantities of monodispersed particles

would be particularly useful.

Recent research by Matijević, et al. [1, 2, 3, 4] indicates that particles of various metal hydrous oxide sols are monodispersed. Indications are that these ferric hydrous oxide sols can be generated in a near spherical shape in the one to three micrometer (μm) diameter region.

The purpose of the research reported herein was to duplicate and vary the techniques of Matijević so as to determine if practical quantities of monodispersed particles of selected sizes could be produced using readily available equipment and straightforward methods. Emphasis was directed to ascertain those parameters or techniques which would increase the sphericity of the particle.

The generation of monodispersed particles has been the objective of considerable research in the past. Early efforts on systems making use of gold [5], selenium [6], silica [7,8,9], silver halides [10], sulfur [11],[12], and barium sulfate [13] have been reported in the literature. Although monodispersed particles were produced they were usually very small. For example, silica particles of 0.1 μm diameter [9], sulfur sols of 0.5 μm diameter [11], and gold particles of 0.02 μm diameter [5] have been reported. Production of silica particles in the 1-2 μm diameter range were reported in one case [8], but particle sizes could not be precisely controlled. Occasionally, a high standard deviation of sizes resulted.

Development of polystyrene latex particles [14] in the 0.09 - 1.1 μm range and polyvinyl toluene latex particles in the 1-6 μm range by Dow Chemical Company personnel permitted generation of aerosols by atomizing dilute suspensions of these particles. However, the residual

stabilizer presents a nuisance background that is especially troublesome when light scattering methods of analysis are used [15]. Portions of the stabilizer which do not contain latex particles are atomized. As the suspension liquid evaporates, the dried stabilizer forms small particles with sizes differing from that of the latex. This distorts the size distribution of the resulting aerosol.

Recent work in the area of metal hydrous oxide sols has opened a new area of essentially monodispered particle generation. Chromium hydroxide hydrosols [1, 16] were produced first, but these spherical particles had a modal diameter of 300 mμ and took up to 21 hours to generate. Copper hydrous oxide sols have been produced [2], but the size distribution varied. Later, aluminum hydrous oxide sols were produced that exhibited very nearly a spherical shape [3, 17]. However, the aging period took up to 48 hours. A number of investigations using ferric hydrous oxides have been reported. Deposits of B-FeOOH crystals by Watson and Cardell [18] showed formation of particles with remarkably uniform sizes. Hydrolytic polymerization of ferric citrate [19] gave spherical particles with a diameter of 72 ± 9 Å which places them in the category of monodispersed particles. In later work on crystal nucleation, Atkinson, et al. [20] varied parameters such as hydrolyzation reaction time, and reaction pH. The particles that were produced were neither spherical nor monodispersed. Following this work with metal hydrous oxide sols, Matijević produced ferric sulfate particles that were indeed monodispersed [4]. Matijević reported that by combining proper molar ratios of $[Fe^{+3}]$ to $[SO_4^{-2}]$, using filtered solutions to assure homogeneous nucleation, and controlling the rate of temperature rise, near spherical, monodispersed,

1 to 5 μm diameter particles could be produced. Reaction times of one to three hours were used. The control of the rate of temperature rise from room to a pre-set reaction temperature was specified as an important variable.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

The simple equipment requirements and the straightforward preparation methods make the Matijević technique a desirable and quick way of producing monodispersed particles. In addition to the chemicals, the equipment required consists of conventional laboratory glassware and a controllable hot plate or heating device. In order to produce monodispersed particles, they must be formed *via* homogeneous nucleation. This requires that both the glassware and the reaction solutions be very clean and free of foreign particles which may cause heterogeneous nucleation.

The chemicals used for the reaction solutions were obtained from Fisher Scientific Company and were USP reagent grade and thus required no further purification. The chemicals included ferric sulfate $Fe_2(SO_4)_3$, ferric nitrate $Fe(NO_3)_3$, sodium sulfate Na_2SO_4, and urea NH_2CONH_2. Chormic acid cleaning solution, hydrochloric acid HCl, and sodium hydroxide NaOH solutions were used for the cleaning of glassware, and a dilute nitric acid HNO_3 solution was used for washing of the particles after reaction. An amyl acetate and nitrocellulose solution was used as a medium for containment of the particles on the specimen grids that were required for electron microscope examination. This solution also served to disperse the particles and aided in the analysis procedure. To assure homogeneous nucleation pyrogen-free distilled water was used in preparing the solutions. According to Zeif and Speights [21], this water has twice

the specific resistivity of double distilled water.

All solution storage bottles and all reaction tubes require rigorous cleaning to avoid contamination of the solutions. The method of cleaning the glassware was that employed by Matijević [4]; it consisted of immersing the glassware in 6M hydrochloric acid for one hour, in chromic acid cleaning solution for one-half hour, and in 6M sodium hydroxide for another half hour. The glassware was then rinsed twice in distilled water and dried in a dust free environment.

A Millipore filter system was used to filter the ferric nitrate, sodium sulfate, ferric sulfate, urea, and nitric acid solutions used in the experimental phase. A 0.45 μm filter served to remove particulate contaminates. The filter system consisted of two Erlynmeyer vacuum flasks in series to assure that no water could be drawn back into the solution being filtered. The filtered solutions were stored in previously cleaned and dried, glass stoppered, pyrex glass jars for later use. Teflon capped pyrex culture tubes which measured 25 x 150 mm were selected as vessels for reaction of the ferric nitrate and sodium sulfate and the reaction of the sodium sulfate and the urea. A simple cardboard stand was constructed to hold the tubes in a beaker filled with mineral oil. A Corning, Model PC-351, hot plate and magnetic stirrer was used to heat and stir the oil bath. Two thermometers were used, one to indicate the temperature in the oil bath and the other the temperature inside one of the culture tubes. This arrangement permitted determination of the temperature lag within the reaction tube. The rate of heating was controlled manually with the hot plate controller.

A conventional test tube centrifuge was employed to separate the

particles from the reaction liquor and washing solution. Centrifugation was accomplished at 3600 RPM in order to assure separation but to avoid packing the particles too tightly which would prevent easy redispersion. Particle examination was done with an electron microscope. A JOEL, JEM-30, transmission electron microscope having magnifications of 2000x, 3000x and 4000x was used. This magnification range is appropriate for observing particles in the 1-3 μm range. Two-hundred mesh carbon-collodion coated copper grids were used for examination of the particles. These grids were coated in a vacuum system and were obtained from the Georgia Tech Engineering Experiment Station. The electron micrographs of the particles were taken with the 35 mm camera that is an integral part of the electron microscope. A calibration grid was obtained from Ernest F. Fullam Inc., Schenectady, N.Y. This calibration grid was photographed at the various magnifications in order to determine particle sizes. Analysis of the particles for particle size distribution was done on a Zeiss Particle Size Analyzer utilizing the electron micrographs. The determination of the particle lattice parameters was accomplished by direct projection of the negatives using a slide projector.

CHAPTER III

PROCEDURE

The procedures in the work done by Matijević, et al. [4] were duplicated except that the rate of heating was manually controlled. This involved the generation of ferric hydrous oxide sol by heating dilute solutions of salts containing Fe^{+3} and SO_4^{-2} ions in a hydrous medium. The temperature of the salt solutions were slowly raised from approximately 22°C (room temperature) to 80°C and the solution was maintained at this temperature for a pre-set period of time. With the rise in temperature the solution becomes supersaturated, nucleation begins, and subsequent particle growth is initiated. Growth continues while the solution is at 80°C. Particle growth was terminated by chilling the solution in an ice bath. Several parameters of sol generation were varied, and the resultant particles were examined for changes in particle size and shape. Parameters varied included pH, solution concentration, ratio of $[Fe^{+3}]$ to $[SO_4^{-2}]$, rate of rise of temperature, and period of growth at 80°C.

A 0.18M ferric nitrate solution and a 0.53M sodium sulfate solution were prepared by weighing reagent grade ferric nitrate and sodium sulfate and mixing each with distilled water. Using a Mettler balance, 18.18 grams of ferric nitrate and 18.82 grams of sodium sulfate were weighed then diluted to 250 mls. in previously cleaned volumetric glassware. The solutions were not checked against a standard since the work by Matijević [4] implied that such accuracy was not necessary. The solu-

tions were immediately filtered through a 0.45 μm Millipore filter and stored in clean, dry, pyrex glass stoppered bottles. The solutions were not used after more than two weeks of storage.

Two tubes were used for each test, and 10 ml. of each solution was pipetted into each tube. These tubes were then submerged into a magnetically stirred oil bath. The oil bath was a 1000 ml. beaker filled with mineral oil which was heated and agitated on the hot plate. The temperature of the bath was raised using the manual control on the hot plate. In using the manual heat control, the attempt to maintain a linear temperature rise usually resulted in temperature increases of 1.4 to 1.7 °C per minute. The temperature of the bath was recorded each minute and once the temperature was at 80°C it was held there for the specific periods of time necessary to produce various particle sizes. The longer the time at 80°C, the larger the particles. After the reaction time at 80°C had expired, the pyrex tube was inserted into an ice bath to retard any further growth. Following a few minutes in the ice bath, the solutions were transferred to previously cleaned and dried test tubes. The tubes then were centrifuged at approximately 3600 RPM to separate the particles. The supernatant solution was poured off, and the particles were redispersed in a few ml. of 0.05 nitric acid solution which gave the same pH as the reaction media; the tubes were then centrifuged once again. This washing with the dilute nitric acid solution was repeated four times to remove the leftover reaction salts which would interfere in the electron microscope examination. The repeated washing also helped remove fines and any undersized growth which would destroy the monodispersity of the particles. The particles were finally poured on glass

slides to be dried.

Preparation for examination under the electron microscope was the next step and followed immediately after the centrifuging and drying of the particles. The techniques followed for electron microscope grid preparation were from Desmond Kay [22] and Orr and DallaValle [23].

Two-hundred mesh copper grids vacuum coated with a carbon-collodion film were provided by the Analytical Instrumentation Lab of the Georgia Tech Engineering Experiment Station. The particles were dispersed on the grids through the use of a five percent by weight nitrocellulose-amyl acetate solution. The cellulose was dissolved in reagent grade amyl acetate and a drop of this solution was placed on the slide with the dried particles. Using another slide, this acetate solution was spread to form a thin coating of the film over the particles. The film was immediately dried by blowing gently on it. The moisture in the breath is important in that it aids in peeling the film off the slide. The film was then cut into grid size sections, and these sections were floated off the slide by slowly dipping the slide into a beaker of distilled water. The grids were then dipped under these floating sections so that the film with the particles adhered to the grid. After drying on filter paper, the grid was ready for examination in the electron microscope.

Following visual examination, selected grids were photographed using the built-in 35 mm camera of the electron microscope. Two techniques were used to aid in the analysis and sizing of the photographed particles. In the first method the particles were sized using the circular aperture of a Zeiss, TGZ3, Particle Size Analyzer. The linear summation mode of the Zeiss Analyzer was employed because the particles appeared

to be very nearly monodispersed.

Because the particles appeared to be cubic rather than spherical in shape, their different linear dimensions would be a function of orientation, hence some question existed as to the validity of this measurement technique. In the second method, the electron micrograph negatives were projected on a large screen using a Kodak, 620, Slide Projector.

Particle dimensions were then measured on the screen and recorded along with the other test parameters. These data were employed in determining particle monodispersity and in obtaining a measure of the relationship between particle size and reaction time. The electron micrograph projections also helped in the study of the affect of parameter variations on the particle characteristics. Other scanning electron micrographs were made to aid in determining particle shape.

CHAPTER IV

RESULTS AND DISCUSSION OF RESULTS

Over twenty-five particle production tests were made during the course of this research. Each was identified by assignment of a number corresponding to the date on which it was made. Where more than one test was made on a given date, successive tests were designated as A, B, C, and D. Appendix A lists all the tests and the reaction parameters for each test. Some difficulty attributed to procedural inexperience occurred during the earlier tests. Once a suitable procedure was established, reasonable consistency existed for the remainder of the tests. Initially, the experiment and particle production tests were based on parameters that according to Matijević [4] produced near-spherical particles. These parameters included (1) the reaction of equal volumes of 0.53 M sodium sulfate and 0.18 M ferric nitrate, (2) a controlled temperature rise of 1.5°C/min, and (3) a terminal temperature of 80°C. for sixty minutes. Although Matijević used an automatic temperature controller to assure a linear temperature rise, a manual temperature control was used for the research reported herein. The temperature rise data for selected tests as presented as Appendix B illustrate the ability for manually maintaining the oil bath temperature rise at 1.5 ± 0.1°C/min. Once the reaction temperature of 80°C. was attained, the temperature controller was capable of maintaining the oil bath at 80°C. without further adjustment. Nearly monodispersed particles were produced in all tests, but no evidence of

spherical particles was noted. The outline of some particles closely approximated a sphere; but, upon closer examination, they proved to be cubes or truncated cubes with opposing corners flattened. The orientation of the cubes and the truncation gave rise to a hexagonal outline. Further, the particle sizes for given reaction periods appeared to be significantly smaller than those reported by Matijević.

Effect of Reaction Time on Particle Characteristics

The parameters which Matijević employed to produce spherical particles of different diameters were adhered to for most of the tests during this research. Tests 11-20A through 1-9B were made with a constant molar ratio of $[Fe^{+3}]$ to $[SO_4^{-2}]$ of 1:2.94, and the temperature rise was held constant at $1.5 \pm 0.1^{\circ}C$/min. during these tests. The reaction temperature of $80^{\circ}C$ was not varied, and no variance of this parameter was attempted during the course of the study. The only variable changed for these tests was the length of time that the solutions were held at $80^{\circ}C$; this period was varied from 45 to 86 minutes. Immediately after formation, the particles were visually examined with the electron microscope; but a more detailed examination and analysis was required to determine if the particles were all the same size and to check the method of production for reproducibility. To accomplish this, a number of electron micrographs were made. Several regions on each grid were photographed so that a wide range of the particles produced in each test could be examined. Figures 1 and 2 are enlarged prints of selected micrographs and show the particle outlines for two different magnifications. In all of the electron micrographs, the particles appeared to be cubic in

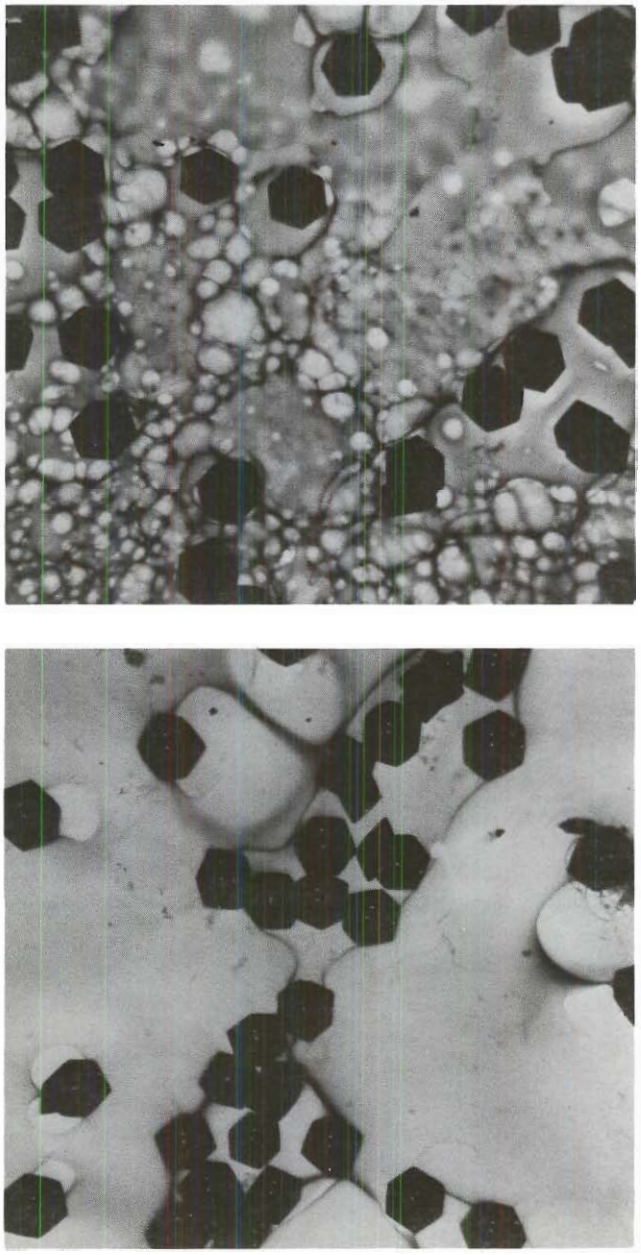

Figure 1. Electron Micrographs of Test No. 1-9B, 2000X

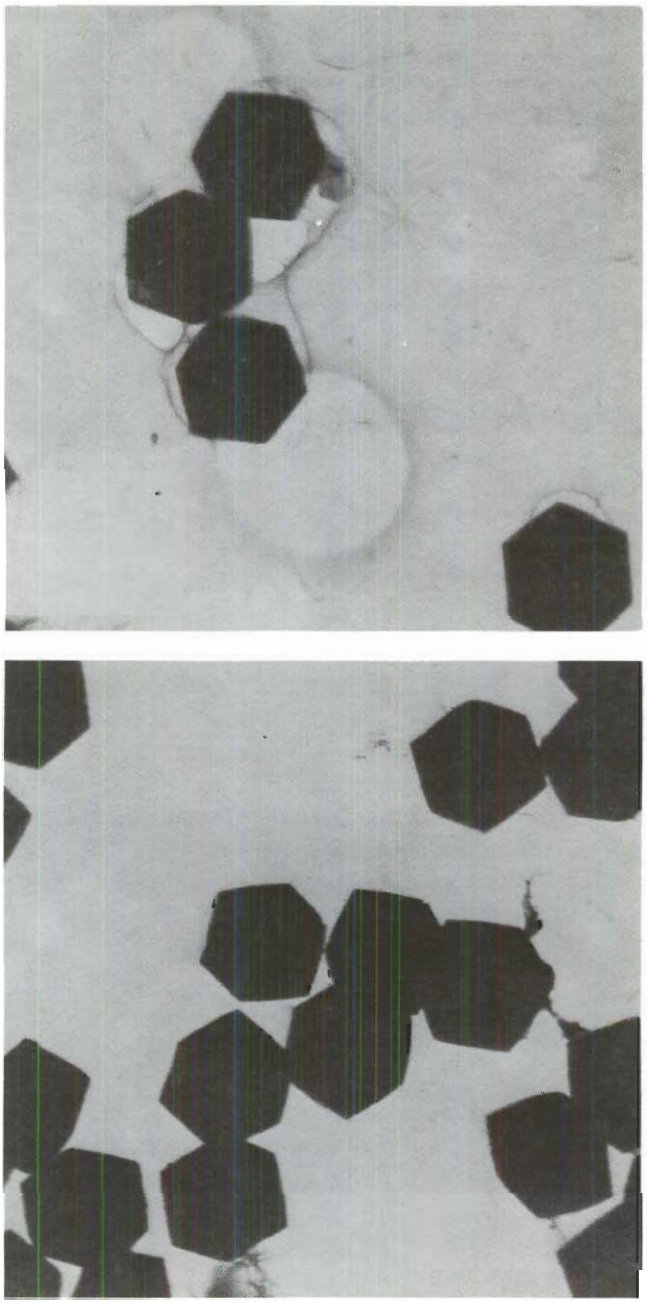

Figure 2. Electron Micrographs of Test No. 1-14A, 4000X

shape with the varied orientations producing hexagonal outlines.

Because of the inability to verify the exact shape of the ferric sulfate particles with the transmission electron microscope, additional micrographs were made with the scanning electron microscope at the Analytical Instrumentation Laboratory of the Georgia Tech Engineering Experiment Station. Particles from Test 1-14A, were examined, and Figure 3 shows two photographic prints of these micrographs. From Figure 3, it can be seen that the particles have a basic cubic shape except that each particle appears to be a truncated cube with opposite corners flattened or missing. Since the particles tend to rest on a flattened corner, they produce an outline that is rhombohedral or hexagonal which is the lattice parameter of ferric sulfate crystals.

Extensive measurements were made on the micrographs of one 86-minute test (1-14B), two separate 80-minute tests (1-9B and 1-14A), one 75-minute test (1-14D), and one 55-minute test (11-20B). The electron micrograph images were projected on a large screen, and the dimensions of the particle edges were measured. The dimensions on the projected images were determined through use of a similarly projected image of a calibration grid. The particular calibration grid used was a 28,800 line-per-inch replica grating. This corresponded to 0.882 μm between each line.

Table 1 shows the reaction time *versus* the apparent cubic dimensions for the four tests, and Figure 4 presents the data in graphical form. As is evident from the straight line fitted to the data, the particle sizes are a linear function of the reaction period. The growth rate suggests that $Fe_3(SO_4)_2(OH)_5$ molecules form and are transported to the surface of

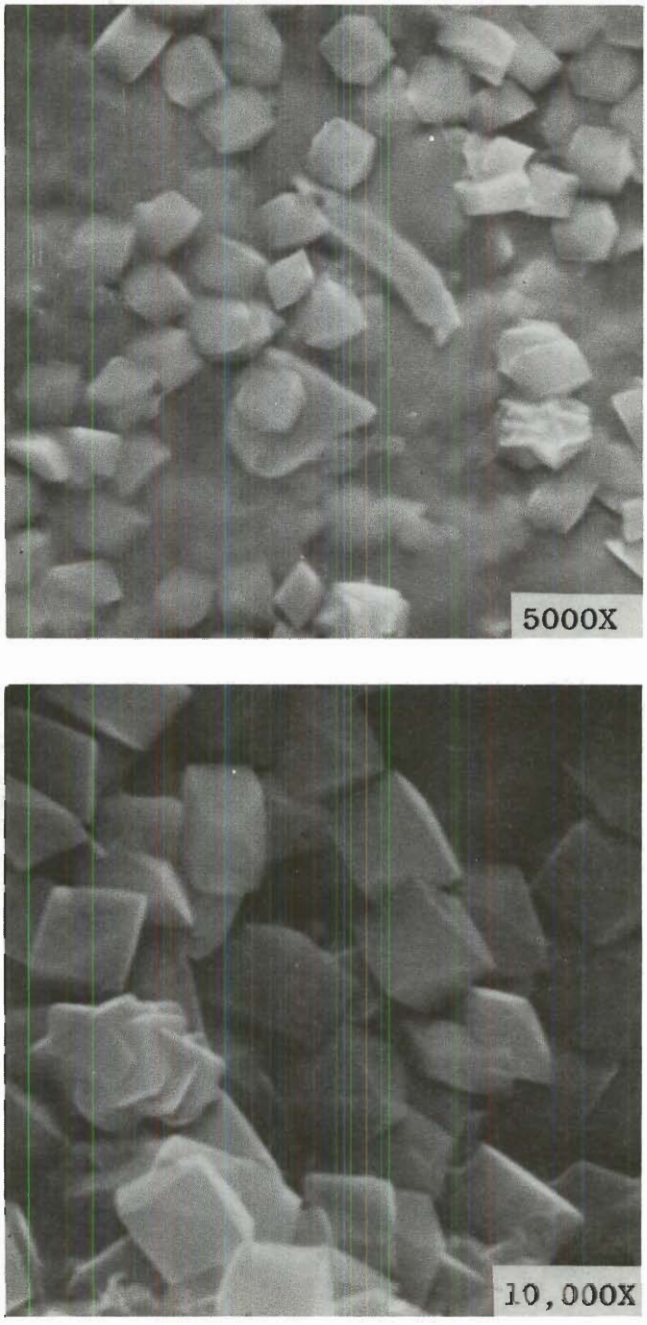

Figure 3. Scanning Electron Micrographs of Test No. 1-14A.

Table 1. Particle Dimensions from Selected Tests

Test No.	Time (min)	Edge Length (μm)
11-20B	55	0.777
1-14D	75	1.43
1-9B, 1-14A	80	1.55
1-14B	86	1.71

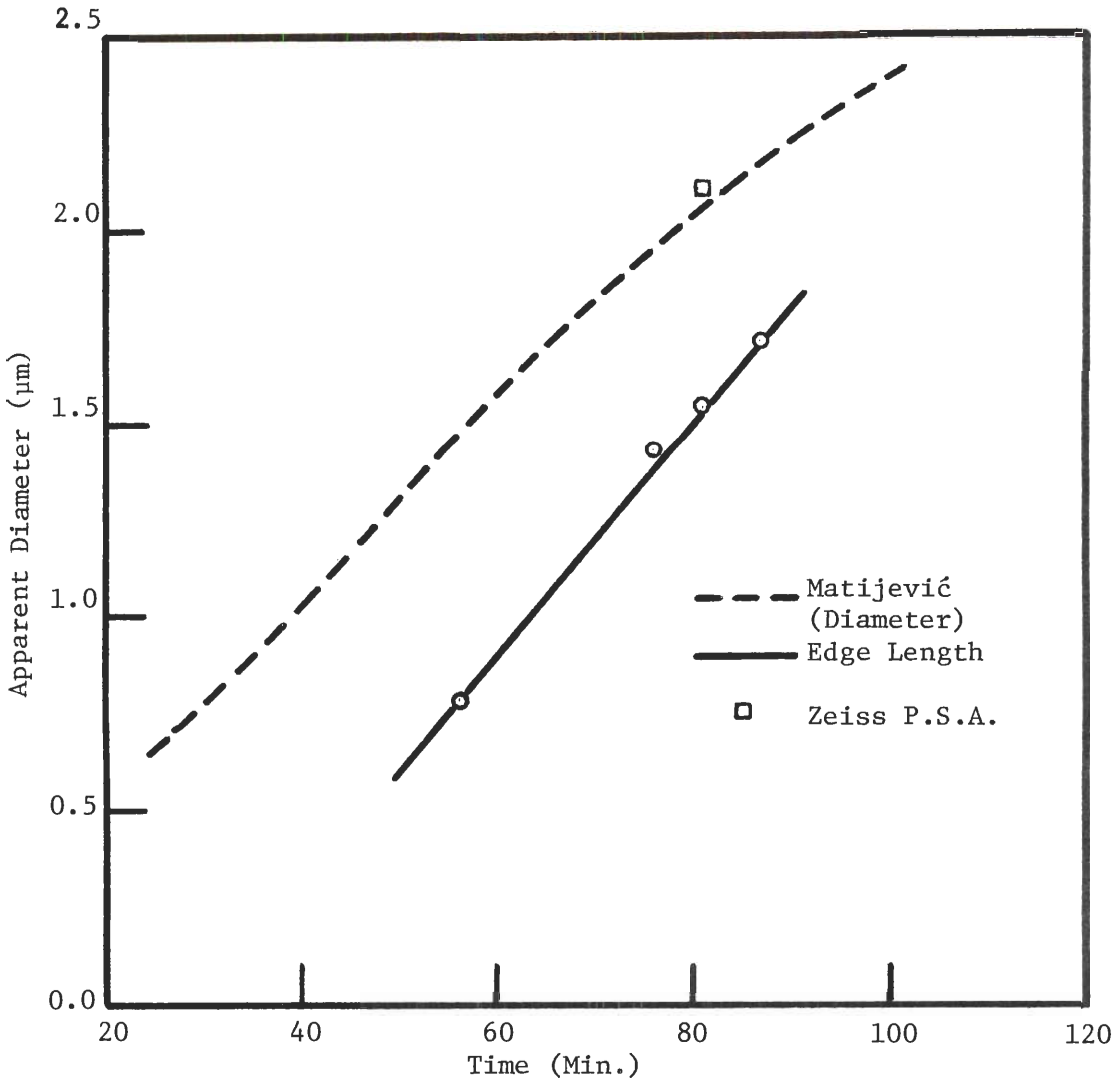

Figure 4. Particle Dimension Versus Reaction Time

an existing particle. The driving force for crystal growth would be the difference in the solution concentration denoted as C(solution) and the crystal surface concentration C(surface). The rate of change of mass would be proportional to the difference in these concentration gradients; hence,

$$\frac{d(\text{mass})}{dt} = KA[C(\text{solution}) - C(\text{surface})]$$

where K is the proportionality constant and A the area of the particle exposed to the solution. Assuming cubic particles and letting R represent an edge then:

$$\frac{d\rho R^3}{dt} = K6R^2[\Delta C],$$

where ρ is particle density. Therefore,

$$\rho \frac{dR^3}{dt} = K6R^2[\Delta C], \text{ and}$$

$$\rho\ 3R^2 \frac{dR}{dt} = K6R^2[\Delta C].$$

For the range shown by the data of Figure 4 it is assumed that the ΔC term remains constant. At the beginning of crystal growth C(surface) is zero and near the end C(solution) becomes small. In these regions ΔC is a non-linear function of time. Assuming the remainder of the growth

period occurs at constant ΔC, the preceding equation becomes

$$\frac{dR}{dt} = \frac{K2}{\rho}[\Delta C] = \text{constant}.$$

Solving for R gives the straight line equation

$$R = at + b.$$

For the data given this equation is evaluated to be

$$R = 0.030509\ t - 0.09,$$

from which the time of growth to a given particle size can easily be predicted. Note the offset of the curve in Figure 4 relative to the data reported by Matijević which is shown for comparison as a dotted line. The probable reason for the offset is that Matijević measured his particle sizes by fitting a circular aperture over the particle image with a Zeiss TGZ3 Particle Analyzer. This technique would indicate a larger particle; that is, it would show the apparent diameter rather than the edge dimensions of the cubes. For the tests reported herein, the dimensions of the cube edges on the projected image are plotted in Figure 4.

In order to compare further the particle dimensions to those reported by Matijević, several micrographs of particles with varied orientations were measured with the Zeiss analyzer by fitting a round aperture over the hexagonal particle contours. Because of the different orientation

of each particle, the measured sizes showed some spread even though the particle edge dimensions indicated that they were essentially monodisperse. This distribution is shown as Figure 5. The mean particle size obtained from the latter measurement technique is shown by the square symbol on Figure 4; its location supports the contention that the offset observed is a function of the measurement technique.

Effect of Molar Ratio and Acidity

Matijević reported that the most critical parameter for obtaining spherical particles was a molar ratio of $[Fe^{+3}]$ to $[SO_4^{-2}]$ of 1:2.94. In order to test this specification, molar ratios of 1:3.10 through 1:3.47 (test numbers 1-13, 1-14A, 1-14C, and 1-20A&B) were investigated. In each case the resultant particles appeared to be cubes, and no hint of spherical formation was observed.

Matijević suggests that the overall reaction for the formation of the major component of the ferric particles is:

$$Fe_2(OH)_2^{+4} + Fe(OH)_3 + 2HSO_4^- \rightarrow Fe_3(SO_4)_2(OH)_5 + 2H^+. \qquad (1)$$

From Equation (1), it can be seen that the reaction takes place in an acidic medium. In order to determine if the pH is a parameter which influences the morphology of the ferric sulfate particles, one milliliter of 0.05M nitric acid solution was added to a reaction tube containing twenty milliliters of the ferric nitrate and sodium sulfate solution prior to heating (test 1-20A). Nitric acid was selected since NO_3^{-1} ions are already present in the ferric nitrate solution. The only observable effect of lower

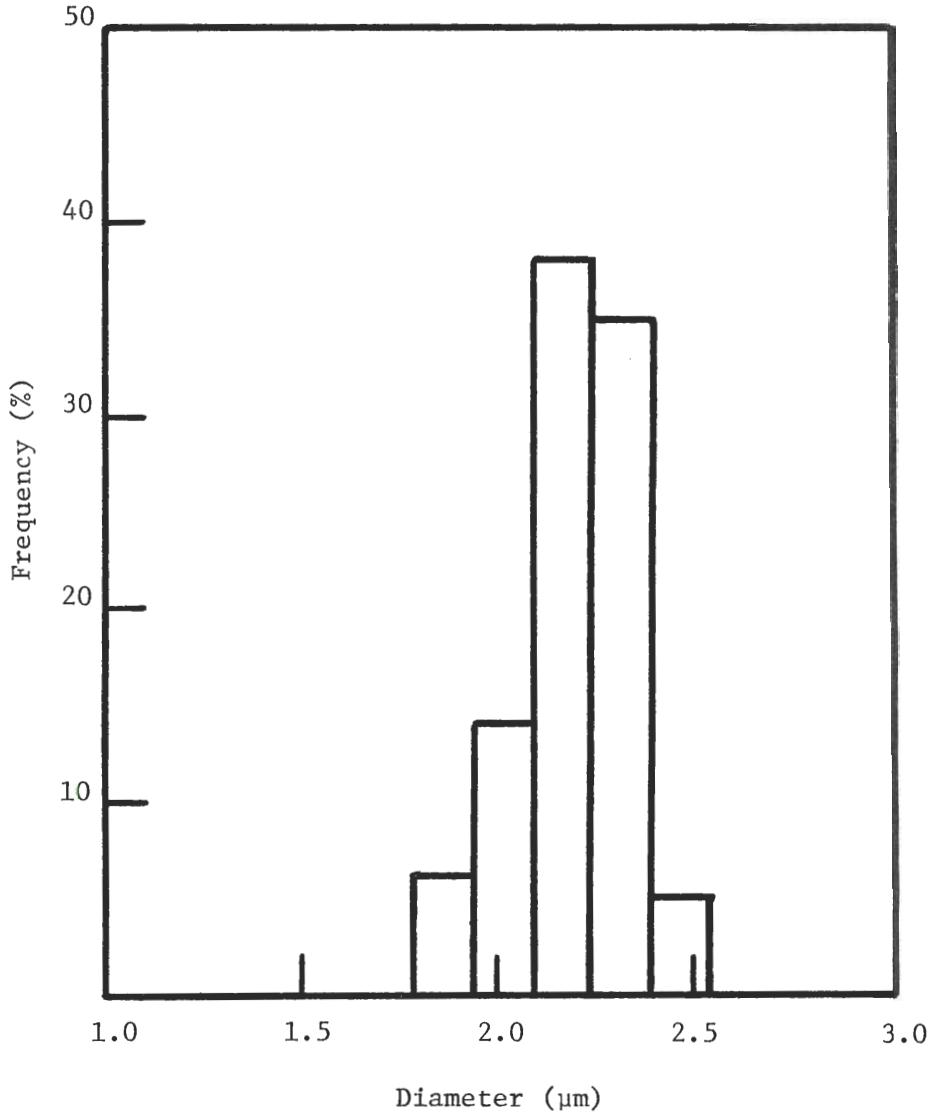

Figure 5. Particle Size Histrogram Obtained From Electron Micrographs of Test No. 1-9B

pH in test number 1-20A was that the particles formed were not cubes. One major dimension was larger than the other, but the difference was not very great. From the results of this limited test it does appear that low pH may influence the morphology of the particles.

Secondary Growth

A number of other variations were noted when Matijević's parameters were altered. For example, in test 11-13 the heating rate was permitted to exceed 1.7°C/min.; and an abundance of secondary growth occurred in addition to the production of cubic ferric sulfate particles. When visually observed in the reaction tube, this growth appeared as a gelatinous porous mass. Upon closer observation with the electron microscope, the secondary growth appeared to be a crystalline structure with a fine needle-like shape. Even after five washings with dilute nitric acid solution, this secondary growth could not be separated from the ferric sulfate particles. Consistently, heating rates of 1.4 to 1.5 °C/min. would initiate secondary growth.

Matijević also formed particles using ferric sulfate and urea similar to the ones formed with the ferric nitrate and sodium sulfate. In this research ferric sulfate and urea solutions were combined in accordance with the same procedure employed in mixing the ferric nitrate and sodium sulfate. In two separate cases the ferric sulfate solution underwent reaction overnight before the heating test with urea could be made. The particles that formed appeared to be the needle-like secondary growth formed in tests where the temperature of the ferric nitrate and sodium sulfate solution was increased at a rate higher than 1.5° C/min. No further

tests were undertaken with ferric sulfate.

Several other tests for producing monodispersed particles resulted in secondary growth. Again the secondary growth appeared to be needle-like crystals that massed together in clumps. In each of these cases, ferric sulfate particles were formed along with the secondary growth. In each case of secondary growth it is to be noted that the reactant solutions were about two weeks old; that is, it had been two weeks since the solutions had been mixed and filtered. For test 12-18 the ferric nitrate storage jar had recrystallized ferric nitrate around the glass stopper. Some of this got into the reaction tube and on this run a massive amount of secondary growth occurred. A possibility as to the cause of the secondary growth phenomena can be obtained from a review of the chemistry of ferric sulfate production. For normal ferric sulfate particle growth, the process is thought to be ferric ion hydrolysis followed by supersaturation of the solution with the rise in temperature, and the subsequent precipitation of ferric sulfate particles. Ferric ions are found to hydrolyze easily at room temperature [25] and form ionic species such as $FeOH^{+2}$, $Fe(OH)_2^{+}$, $Fe(OH)_2^{+4}$, and $Fe_3(OH)_4^{+5}$. In related work Matijević [26] found that in the production of chromium oxide sol particles, $Cr(OH)_3$ played an important role in the precipitation process. It was found that a strand-like material of $Cr(OH)_3$ acts as a precursor or heteronucleating agent. Ferric hydroxide formed from the hydrolysis of ferric ion is also thought to play a similar role in ferric hydrous particle production. Also, it has been reported that ferric hydroxide has a strong tendency to form supersaturated solutions [27]. Not much is known about the high temperature hydrolysis of ferric ions, but it is known that heating salt

solutions normally accelerates metal hydrolysis. Matijević [4] reported the presence of sulfate ions speeds the condensation of the hydrolyzed ferric ions, and this may be the reason ferric hydrous sols form particles in such a short time (60 to 90 minutes). Recalling equation (1) and considering the suggested overall mechanism, it appears that the solution becomes more acidic as more particles precipitate due to the evolution of H^+ ions. Research on iron solutions by Sillin and Martell [29] showed that in acidic solutions the ferrous sulfate ($FeSO_4^+$) ion dominates. This provides a clue into secondary growth. Examination of the crystal structure of ferric and ferrous sulfate shows that ferric sulfate ($Fe(SO_4)_3$) has a basic rhombohedral or hexagonal lattice parameter whereas ferrous sulfate ($FeSO_4)\cdot H_2O$ has a monoclinic or elongated needle-like shape. If the ferric ions undergo reduction and form ferrous ions and if the particles form and the pH drops, then the needle-like ferrous sulfate would form in the later stages of the reaction.

Suitability for Aerosol Generation

The next phase of the research involved checking the particles for storage and for use in test aerosol generation. Studies that involve the inhalation of insoluble particles usually require a method for dispersing the particles in a dry powder form. This could involve blowing air through a loose mass of dry powder. To determine if particles could be produced as a loose mass of dry powder, particles were formed and washed several times to remove unreacted salts which might crystalize out upon drying; then the particles were dried. In every case the particles did not dry as a loose powder but stuck together to form a hard rigid crust. Attempts to sepa-

rate the particles caused them to break, indicating that they were fairly brittle in character. This indicates also that the particles would be difficult to prepare for use in a dry dispersion test where monodispersity was needed.

Test aerosols also can be formed by atomizing particles from a liquid suspension. To test this possibility, the ferric sulfate particles were dried in test tubes and then attempts were made to redisperse them in various solutions. Solutions tried were distilled water, 0.05M nitric acid, methanol, and isopropanol. The polar solvents such as the alcohols had no effect whatsoever on the particles. The nitric acid and distilled water readily re-dispersed the particles. The nitric acid solution was found to destroy the particles after a long period of storage. The distilled water had no destructive effect on the particles. After one month's storage in distilled water, the particles could be re-dispersed easily and still exhibit their basic cubic shape. A few particles did exhibit some breaking because of the agitation they received daily. From this test it appears feasible to store the particles in distilled water and to use them for aerosol generation.

Large Scale Particle Production

The important parameters for ferric sulfate particle production were the heating rate, the reaction time at a preset value of 80°C, the ratio of $[Fe^{+3}]$ to $[SO_4^{-2}]$, the reaction pH, and the initial filtering of foreign particles larger than 0.45 μm. It should be possible to duplicate these parameters for large scale production of monodisperse ferric sulfate particles. No difficulty would be expected for the mixing and

filtering of larger volumes of the reactant solutions. The procedure would be essentially the same as that described in Chapter III except that greater volumes and larger equipment would be employed. Since a molar ratio of 1:2.94 produced a monodispersed sol, equal volumes of 0.53M sodium sulfate and 0.18M ferric nitrate could be combined just prior to reaction. The pH control poses no problem because the reaction adjusts its own pH. Because of the dominant effect of pH on the formation of monoclinic ferrous sulfate, care would have to be taken to use only fresh solutions to insure a minimum of ferrous ion. The only reaction parameter that may be difficult for increased reaction volumes would be the necessity for assuring a consistent temperature throughout the solution during reaction. It was found that the heating rate played an important part in particle formation, and the length of time at 80°C was the deciding factor for obtaining a given size particle.

The reaction must proceed without hot and cold spots which could affect the size of the particles. It is recommended that increased reaction volume be obtained by constructing a reactor of coiled tubing, perhaps of pyrex glass, which could be filled with a pre-mixed solution of ferric nitrate and sodium sulfate. The coil then would be immersed in a heating bath that was regulated with a linear temperature controller. The entire length would have to be heated and maintained at the proper temperature with very little variation anywhere in the tube. The heating bath would have to be provided with a suitable agitation mechanism to assure that no hot or cold spots formed anywhere along the immersed tube. The tube could be emptied, rinsed in cleaning solution, rinsed in distilled water, and dried. Then the reaction could be repeated for the same length of

time. The more reaction volume needed, the longer the network of tubes would have to be. Also, more heat would be required to maintain a constant rate of temperature rise and a constant reaction temperature. It is suggested that 25 mm tubing be used initially since this is the diameter of the reaction tubes used in this research.

The large scale production of ferric sulfate particles appears feasible provided the heating problem can be handled without excessive and elaborate equipment. A tendency for secondary growth was noticed when old solutions or contaminated apparatus were employed. Because of this, cleanliness should receive special attention, and fresh solutions should be used for large scale particle production. Because of the excellent reproducibility from test to test for a given set of parameters, large scale production of specific particle sizes could be accomplished as needed with a batch type setup. This would preclude the necessity for a large production capability and long storage times.

CHAPTER V

CONCLUSIONS

The conclusions resulting from this work may be summarized as follows:

1. Essentially monodispersed ferric sulfate particles can be generated with good particle size reproduction.

2. Because of the linear relationship between reaction time and particle size, predetermined particle sizes can be generated.

3. A small change in the ratio of $[Fe^{+3}]$ to $[SO_4^{-2}]$ caused little change in either particle morphology or size.

4. For the various molar concentrations tested and for reaction times up to 86 minutes, spherical particles were not produced. Instead, cubical or truncated cubical particles were the predominate shapes.

5. Ferric sulfate particles can be stored in distilled water for reasonable periods of time and appear to be suitable for test aerosol generation.

6. Ferric sulfate particles tend to adhere and even to fuse to one another when dried and, therefore, are not suitable for dry dispersion.

7. Secondary growth tends to occur if solutions are premixed and stored over periods exceeding 1-2 weeks.

8. If the initial temperature rise rate is too high, secondary growth is enhanced.

9. Secondary growth appears to arise from the reduction of ferric

ion to ferrous ion and to result in a predominance of ferrous sulfate particles.

10. Monodispersed particles of various sizes can be reproduced using relatively simple methods and equipment.

11. Particular attention to cleanliness is necessary for consistent particle production.

12. The growth rate for the range studied follows the equation $R = 0.030509\ t - 0.90$, where R is the edge length in micrometers and t the time in minutes.

CHAPTER VI

RECOMMENDATIONS

As a result of this research, a number of recommendations can be made as follows:

1. Additional tests with reaction times exceeding 80 to 90 minutes should be performed in order to determine if particles with greater sphericity can be formed.

2. Tests with diluted reaction solutions can be performed to determine if the growth of particle agglomerates can be reduced.

3. Atomizing tests should be performed with ferric particles in order to determine the feasibility of using them as monodispersed test aerosols.

4. Additional studies should be performed with aluminum and chromium sols to determine if they might be produced on a larger scale also.

5. Additional tests on metal hydrous oxide sol formation should be undertaken with the aid of a linear temperature programmer since the rate of heating plays an important role in particle formation and in secondary growth.

APPENDIX A

LIST OF HYDROUS OXIDE SOL TESTS

Table 2. Reaction Parameters for Ferric Hydrous Oxide Sol Production

Test No.	Heating Rate (°C/M)	Reaction Time (Min.)	Molar Ratio	Reaction Volume (ml)	Comments
11-10	--	--	--	--	$FeSO_4$ + UREA ($FeSO_4$ formed precipitate overnight; no heat applied)
11-13	1.7	61	1:2.94	20	Secondary growth appeared
11-20A	1.4	45	1:2.94	20	Cubic shaped particles visually observed in electron microscope
11-20B	1.4	55	1:2.94	20	Transferred particles to grids
11-21	1.5	43	1:2.94	20	Transferred particles on grids--particles very small
11-25A	1.6	56	1:2.94	20	Bad amyl acetate caused deformed grid structure
11-25B	1.6	62	1:2.94	20	Bad amyl acetate caused deformed grid structure
12-8	1.5	68	1:2.94	20	Insufficient wash (1 wash). Sodium nitrate crystals formed.
12-9A	1.5	52	1:2.94	20	Used pipette for more precise molar ratio
12-9B	1.5	52.5	1:2.94	20	Uneven heat rate gave very small particle
12-10	1.5	66	1:2.94	20	Very good cubes. Particles washed 3 times.

Table 2. (continued)

Test No.	Heating Rate (°C/M	Reaction Time (Min.)	Molar Ratio	Reaction Volume (ml)	Comments
12-11	1.5	72	1:2.94	20	Much secondary growth. Rate was 1.9 ∿ 5 min., old solutions
12-14	1.5	66	1:2.94	20	Secondary growth, old solutions
12-18	1.5	66	1:2.94	20	Much secondary growth, old solutions--dried on glass top
1-7	1.5	66	1:2.94	20	No grids available, visually observed on old grids, particles appeared good.
1-8A	1.5	68.5	1:2.94	20	No grids available, visually observed on old grids, particles appeared good.
1-8B	1.5	73	1:2.94	20	No grids available, visually observed on old grids, particles appeared good.
1-9A	1.5	75	1:2.94	20	No grids available, visually observed on old grids, particles appeared good.
1-9B	1.5	80	1:2.94	20	Very good and clear, prepared grids for photography
1-13	1.4	80	1:3.53	80	80 ml. in a Erlynmeyer flask, old Fe solution - much secondary growth
1-14A	1.4	80	1:2.94	20	Good monodispersed cubical particles
1-14B	1.4	86	1:2.94	20	Good monodispersed cubical particles

Table 2. (continued)

Test No.	Heating Rate (°C/M)	Reaction Time (Min.)	Molar Ratio	Reaction Volume (ml)	Comments
1-14C	1.4	75	1:3.47	20	Good monodispersed cubical particles
1-14D	1.4	75	1:2.94	20	Good monodispersed cubical particles
1-20A	1.4	70	1:3.46	20	Added H^+, good monodispersed, almost cubical particles
1-20B	1.4	63	1:3.27	20	Good monodispersed cubical particles

APPENDIX B

HEATING RATES FOR SELECTED TESTS

Table 3. Temperature Rise Rate; 20.5°C to 80°C; Test Nos. 1-8A and 1-8B.

Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)
0	20.5	15	43.0	24	56.0	33	69.0
5	27.0	16	44.9	25	57.5	34	70.4
7	32.0	17	47.1	26	59.5	35	72.0
8	34.5	18	49.2	27	61.1	36	73.5
9	36.8	19	50.5	28	63.0	37	75.1
10	38.0	20	51.0	29	64.5	38	76.9
12	40.0	21	52.0	30	65.8	39	78.8
13	40.8	22	53.6	31	67.0	39.75	80.0
14	41.8	23	54.8	32	68.0		

Notes: (1) Reaction Time for Test No. 1-8A was 69 minutes.

(2) Reaction Time for Test No. 1-8B was 73 minutes.

(3) Average temperature rise rate was 59.50°C ÷ 39.75 min. = 1.4968°C/min.

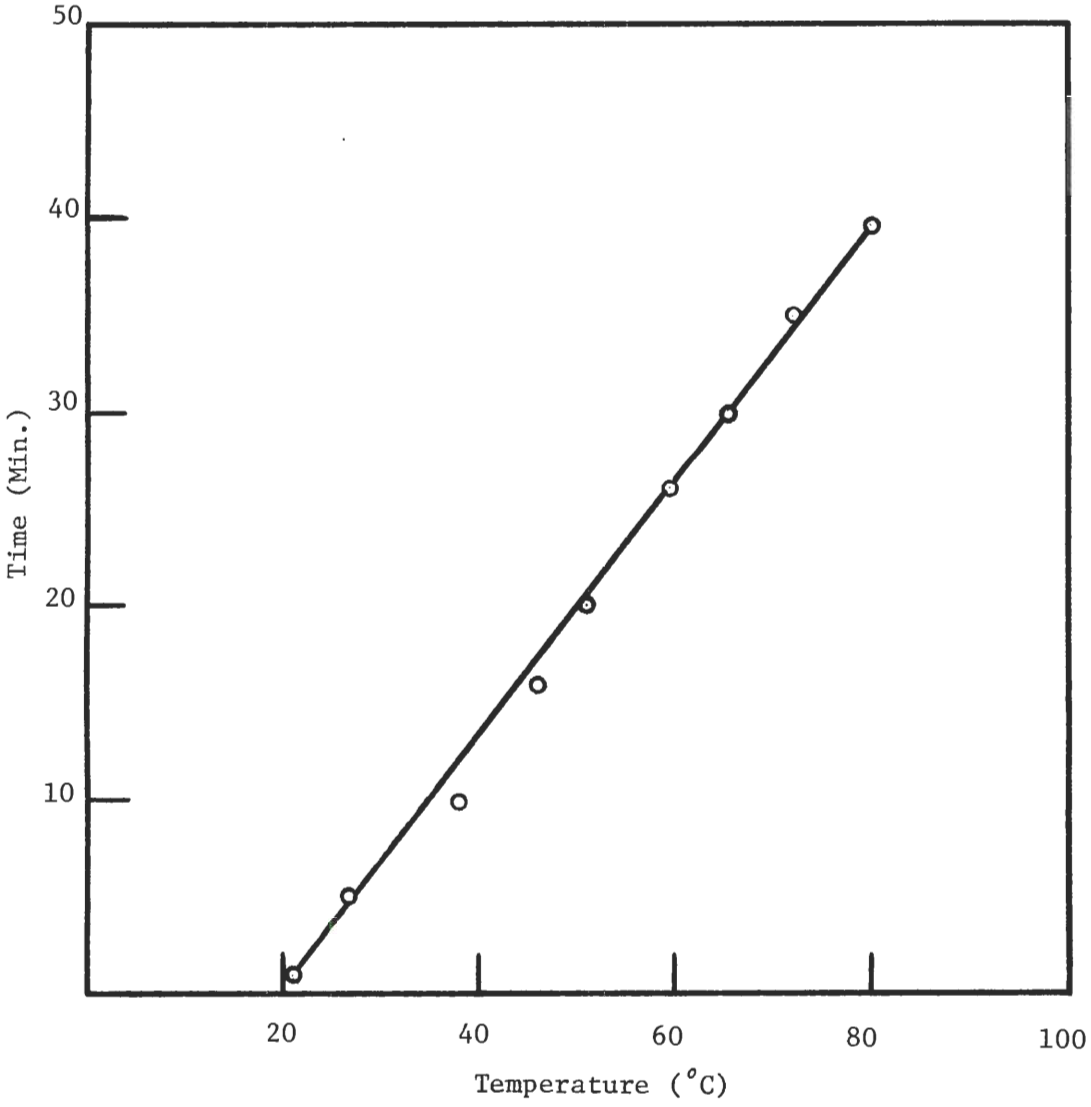

Figure 6. Initial Heating Rate for Test Nos. 1-8A and 1-8B

Table 4. Temperature Rise Rate; 21.8°C to 80°C; Test nos. 1-9A and 1-9B.

Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)
0	21.8	11	39.6	20	53.5	32	67.0
3	24.4	12	40.9	21	54.1	33	68.6
4	26.6	13	42.1	22	54.9	34	70.1
5	29.0	14	43.4	24	56.6	36	73.7
6	31.1	15	44.9	25	58.0	37	75.1
7	33.4	16	46.4	26	59.8	38	77.0
8	35.1	17	48.0	27	61.2	39	78.6
9	37.0	18	50.0	28	61.9	39.92	80.0
10	38.2	19	52.0	30	63.7		

Notes: (1) Reaction Time for Test No. 1-9A was 75 minutes

(2) Reaction Time for Test No. 1-9B was 78 minutes

(3) Average temperture rise rate was 58.20°C ÷ 39.92 min. = 1.458°C/min.

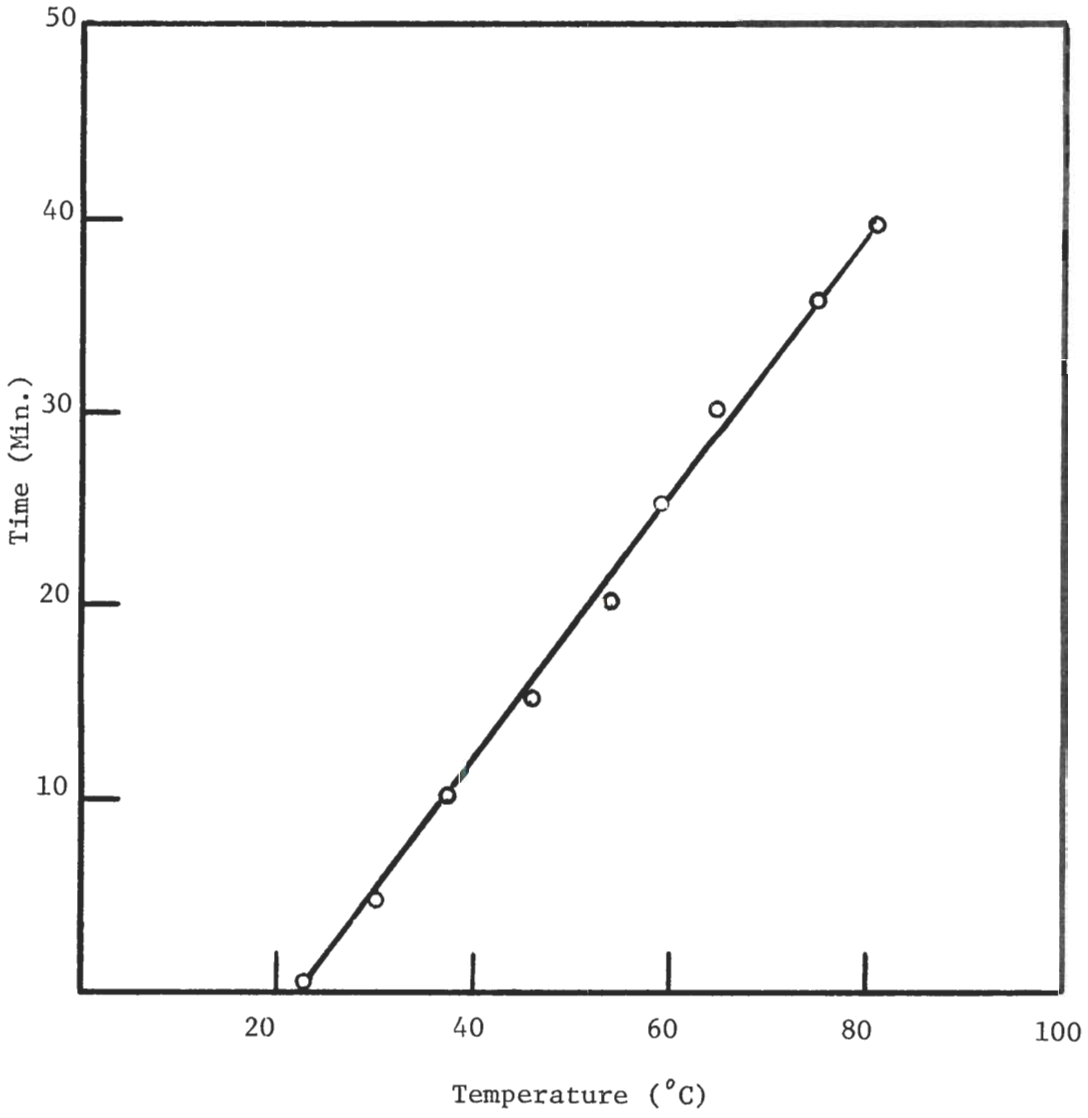

Figure 7. Initial Heating Rate for Test Nos. 1-9A and 1-9B

Table 5. Temperature Rise Rate; 24°C to 80°C; Test No. 12-10

Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)
0	24.0	13	43.6	23	59.0	31	69.5
3	27.0	14	45.6	24	59.8	32	71.0
4	29.0	15	47.1	25	60.0	33	73.0
5	30.9	16	48.7	26	61.0	34	75.0
7	34.1	18	50.9	27	62.5	35	76.5
8	35.9	19	51.9	28	64.0	36	78.0
9	37.0	20	53.0	29	65.7	37	79.5
10	38.5	21	55.0	30	68.2	37.4	80.0
11	40.1						

Notes: (1) Reaction Time for Test No. 12-10 was 66 minutes.

(2) Average temperature rise rate was 56°C ÷ 37.4 min. = 1.497°C/min.

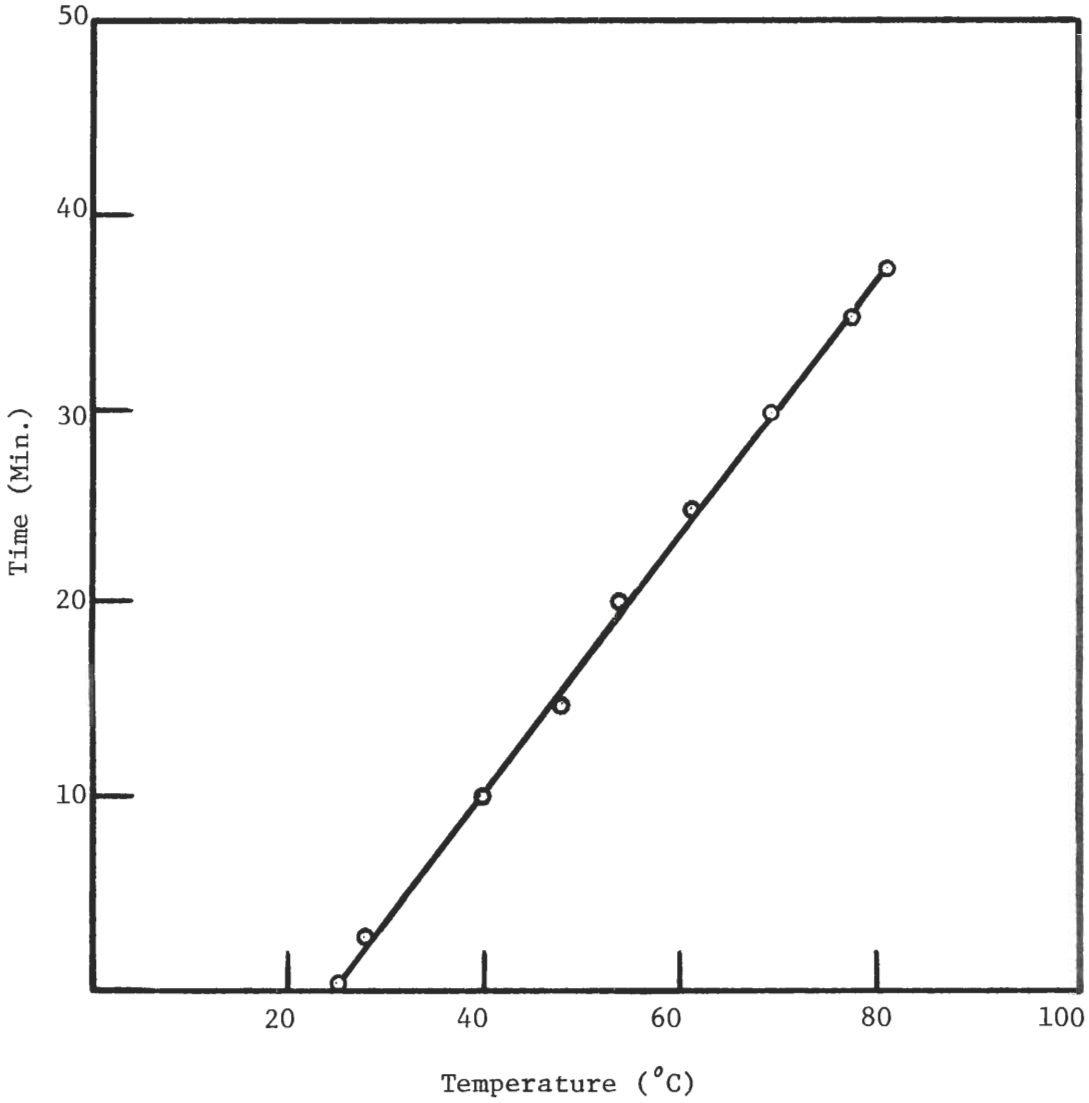

Figure 8. Initial Heating Rate of Test No. 12-10

Table 6. Temperature Rise Rate; 25°C to 80°C; Test Nos. 1-20A and 1-20B.

Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)	Time (min)	Temp. (°C)
0	25.0	11	39.7	22	56.7	32	70.2
2	25.8	12	41.3	23	58.0	33	71.9
3	27.0	13	43.2	24	59.0	34	73.2
4	29.1	14	45.0	25	60.0	35	74.3
5	31.2	15	46.8	26	61.8	36	76.0
7	34.5	16	48.0	29	66.4	37	77.8
8	35.5	17	48.8	30	68.0	38	79.2
9	36.7	19	51.2	31	69.0	38.5	80.0
10	38.0	21	55.0				

Notes: (1) Reaction Time for Test No. 1-20A was 70 minutes.

(2) Reaction Time for Test No. 1-20B was 63 minutes.

(3) Average temperature rise rate was 55.0°C ÷ 38.5 min. = 1.43°C/min.

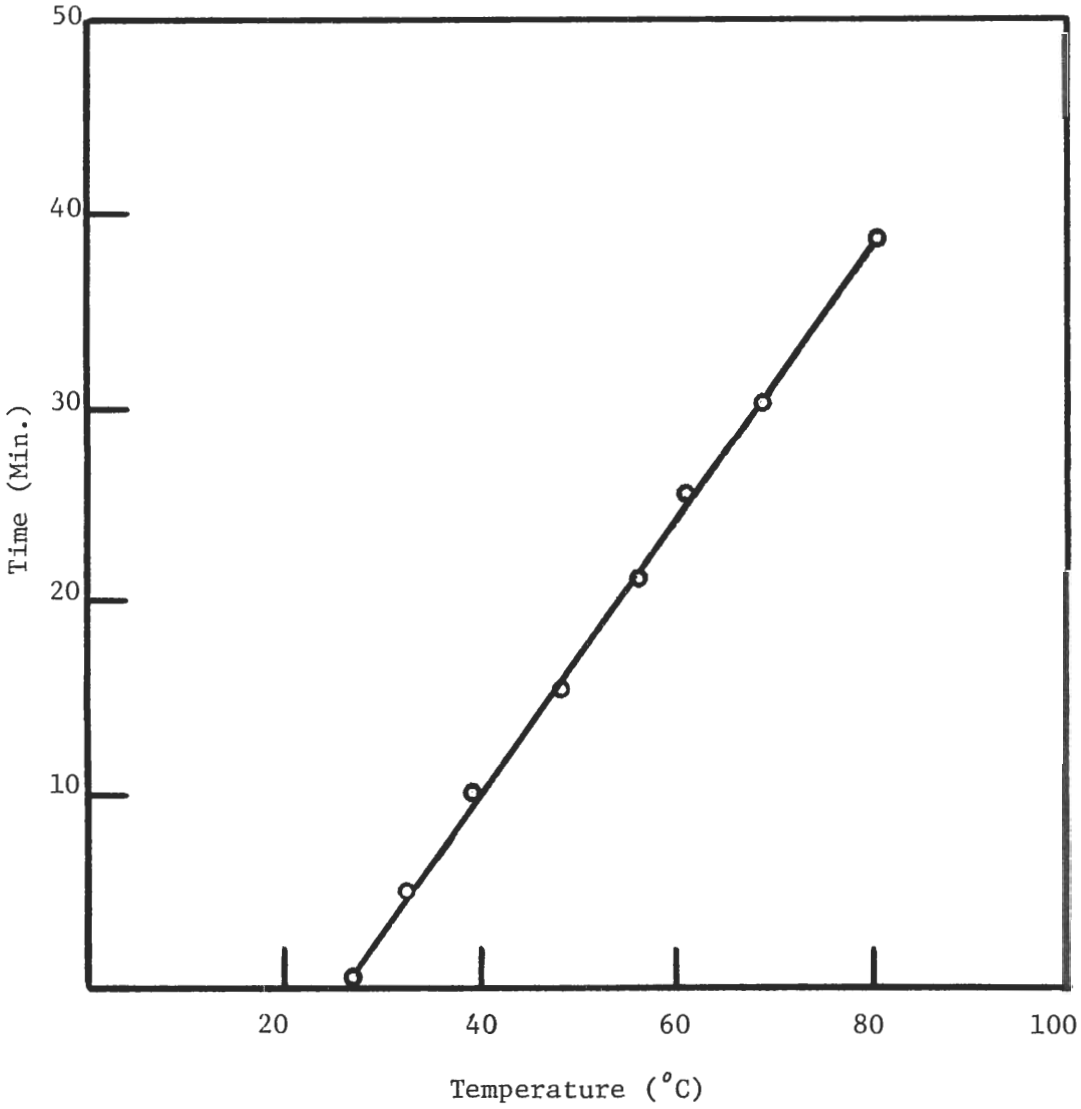

Figure 9. Initial Heating Rate for Test Nos. 1-20A and 1-20B

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